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POLYNITRO POLYCYCLIC CAGE COMPOUNDS

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March 1992

Interim Report

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92-15521



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**PHILLIPS LABORATORY
Propulsion Directorate
AIR FORCE SYSTEMS COMMAND
EDWARDS AIR FORCE BASE CA 93523-5000**

FOREWORD

This interim report was submitted by the University of Dayton Research Institute, Dayton OH for contract F04611-88-C-0020 with the Phillips Laboratory (AFSC), Edwards AFB CA 93523-5000. PL Project Manager was Jeffrey W. Gilman.

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REPORT DOCUMENTATION PAGE

*Form Approved
OMB No. 0704-0168*

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project 0704-0168, Washington, DC 20503.

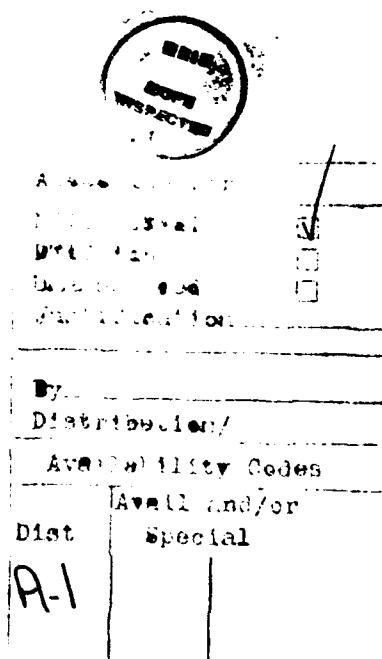
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED	
	March 1992	Interim Report 11/1/89 to 4/30/91	
4. TITLE AND SUBTITLE		5. FUNDING NUMBERS	
POLYNITRO POLYCYCLIC CAGE COMPOUNDS		C: F04611-88-C-0020 PR: 921C TA: 007S	
6. AUTHOR(S)			
Suresh C. Suri			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)		8. PERFORMING ORGANIZATION REPORT NUMBER	
University of Dayton Research Institute 300 College Park Dayton, OH 45469		UDR-TR-91-20	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
Phillips Laboratory (AFSC) Edwards AFB, CA 93523-5000		PL-TR-91-3089	
11. SUPPLEMENTARY NOTES			
<u>COSATI Codes: 07/03</u>			
12a. DISTRIBUTION/AVAILABILITY STATEMENT		12b. DISTRIBUTION CODE	
Approved for public release: distribution is unlimited.			
13. ABSTRACT (Maximum 200 words)			
Treatment of 1, 8, 9, 10-tetrachloro-3 α , 6 α -dihydroxy-11,11-dimethoxytricyclo [6.2.1.0 ^{2,7}] undec-4,9-diene and 1,7,8,9-tetrachloro-3 α -hydroxy-10,10-dimethoxy[5.2.1.0 ^{2,6}]dec-4,8-diene with potassium-t-butoxide/t-butanol furnished two new tetracyclic compounds 1,8,10-trichloro-11,11-dimethoxy-3 α -hydroxytracyclo[6.2.1.0 ^{2,7,04,10}]undec-5-ene-9-one and 1,7,9-trichloro-8,8-dimethoxytracyclo[5.3.0.0 ^{2,6,05,9}]dec-3-en-10-one respectively via base eliminative cyclization.			
14. SUBJECT TERMS		15. NUMBER OF PAGES	
Pentanitrobishomocubane, Favorskii ring contraction, (continued on next page)		18	
		16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT		18. SECURITY CLASSIFICATION OF THIS PAGE	
Unclassified		Unclassified	
19. SECURITY CLASSIFICATION OF ABSTRACT		20. LIMITATION OF ABSTRACT	
Unclassified		Unclassified	

14. Subject Terms continued...

exo-2-carbomethoxy-tricyclo[5.2.2.0^{2,6}]deca-3,8-diene-5-one, 1,2,3,4-Tetrachloro 1,4,4 α ,8 α -tetrahydro-9,9-dimethoxy-endo-1,4-methanonaphthalene-5,8-dione, 1,8,9,10-tetrachloro-3 α ,6 α -dihydroxy-11,11-dimethoxytricyclo[6.2.1.0^{2,7}]undec-4,9-diene, 1,7,8,9-tetrachloro-3 α -hydroxy-10,10-dimethoxy[5.2.1.0^{2,6}]dec-4,8-diene, 1,8,10-trichloro-11,11-dimethoxy-3 α -hydroxytetracyclo[6.2.1.0^{2,7,0^{4,10}] undec-5-ene-9-one, 1,7,9-trichloro-8,8-dimethoxytetracyclo[5.3.0.0^{2,6,0^{5,9}]dec-3-en-10-one.}}

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SUMMARY

The objective of this project is to synthesize advanced propellant ingredients of the propulsion system. This task is divided into two categories: (a) Synthesis of new strained molecules; (b) Study of thermochemical properties of new strained molecules.

This report covers the efforts towards synthesis of new pentanitrobishomocubane and its isomer. During the course of this synthetic endeavor a novel base-promoted eliminative cyclization was observed which lead to the synthesis of two new functionalized strained ring systems: Tetracyclo[6.2.1.0^{2,7}.0^{4,10}]-undecane and Tetracyclo[5.3.0.0^{2,6}.0^{5,9}]decane.

INTRODUCTION

Most current research activities in rocket propulsion have been with the pursuit of improving specific impulse, high-density material and improved handling properties of propellant ingredients. Cage molecules, a new class of energetic materials¹, are of interest as additives in fuels and propellants. These compounds are advantageous because of their compact structure and incorporation of a high level of molecular strain. It is reasonable to assume that highly compact cage molecules provide high densities. Indeed, this assumption has been confirmed both by experiments and by the results of theoretical density calculations. The compactness plays an important role where net volumetric heat of combustion must be maximized². The potential usefulness of such high energy, high density compounds has also captured the attention of the explosive community. Performance criteria for these molecules include detonation pressure and detonation velocity, which vary with cage systems and the number of nitro-substituents. Polycyclic polynitro cage compounds may be useful as a replacement for aluminum in minimum smoke missiles. HMX is currently used; however, it is more sensitive to detonation in comparison to some of the cage compounds. This class of energetic materials not only has potential military applications, but it is also synthetically challenging.

OBJECTIVE

Suggested molecules on the basis of theoretical specific impulse (ISp) studies shall be synthesized using inexpensive starting materials. Once these molecules are synthesized and characterized, their heat of formation shall be determined experimentally. These compounds shall be mixed with other propellant ingredients to determine the effectiveness of the new propellant system.

The synthesis of three nitro and four-nitro analogs of bishomocubane were reported in the literature^{3,4}. One of the initial objectives was to synthesize pentanitrobishomocubane, which has never been reported in literature. Synthesis of the five-nitro bishomocubane was also desired to study the effect of an additional nitro group on the density and explosive properties of these molecules. While some of the chemical methodology established in the chemical literature for polycyclic polynitro cage molecules could be used in the synthesis of pentanitrobishomocubane, the synthetic complexity of adding nitro groups to the bishomocubane system demanded a new approach for the five nitro system.

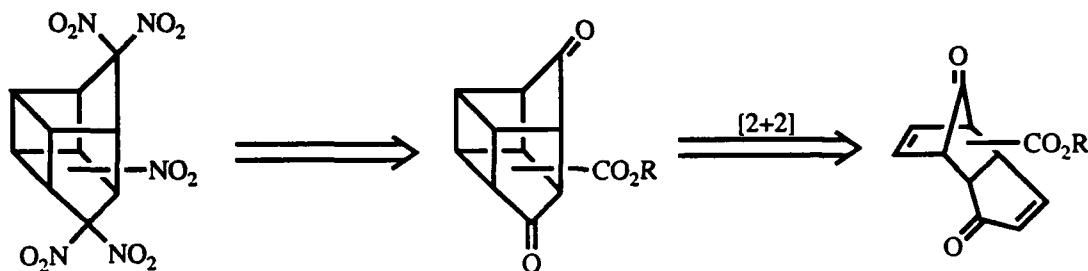
SYNTHETIC APPROACHES FOR PENTANITROBISHOMOCUBANES

A retrosynthetic analysis for the synthesis of pentanitrobishomocubane is given below. It has been established³ that a ketone could be elaborated into a geminal di-nitro species, while a carbomethoxy group could serve as a precursor to a single nitro group^{5,6}.

Two possible routes (A and B) to pentanitrobishomocubane are given in Schemes 1 and 2 respectively. The proposed approach, Route A, involves the Diels Alder adduct 2⁷ of cyclopentadiene and p-benzoquinone. Treatment of 2 with 30% H₂O₂ -10% aq Na₂CO₃ is envisioned to afford the chemoselective epoxidation⁸ to furnish 3. Subsequent reaction of 3 with NaOH-MeOH yields the Favorskii ring contraction product 4⁹. Stereoselective reduction of 4 with NaBH₄-CeCl₃ followed by [3, 3] sigmatropic rearrangement of intermediate allylic alcohol 5 gives 6¹⁰. Allylic oxidation of 6, an unestablished conversion, yields the allylic alcohol 7.

Pyridinium chlorochromate (PCC) oxidation of 7 produces the enone 8, followed by [2+2] photocycloaddition to give the caged product 9.

RETROSYNTHETIC PERSPECTIVE



Route B begins with the Diels Alder reaction of p-benzoquinone [1] and tetrachlorocyclopentadiene dimethyl acetal 11. Dechlorination of the adduct 12¹¹ by Winstein's procedure¹² is expected to give the dechlorinated species 13. Chemoselective epoxidation with 30% H₂O₂ - 10% aq Na₂CO₃ yields the epoxide 14. Favorskii ring contraction of 14 mediated by sodium hydroxide/methanol (NaOH, MeOH) affords the enone 15. Photocycloaddition of 15 produces the caged compound 16 which can be deprotected and further elaborated to the pentanitrobishomocubane system.

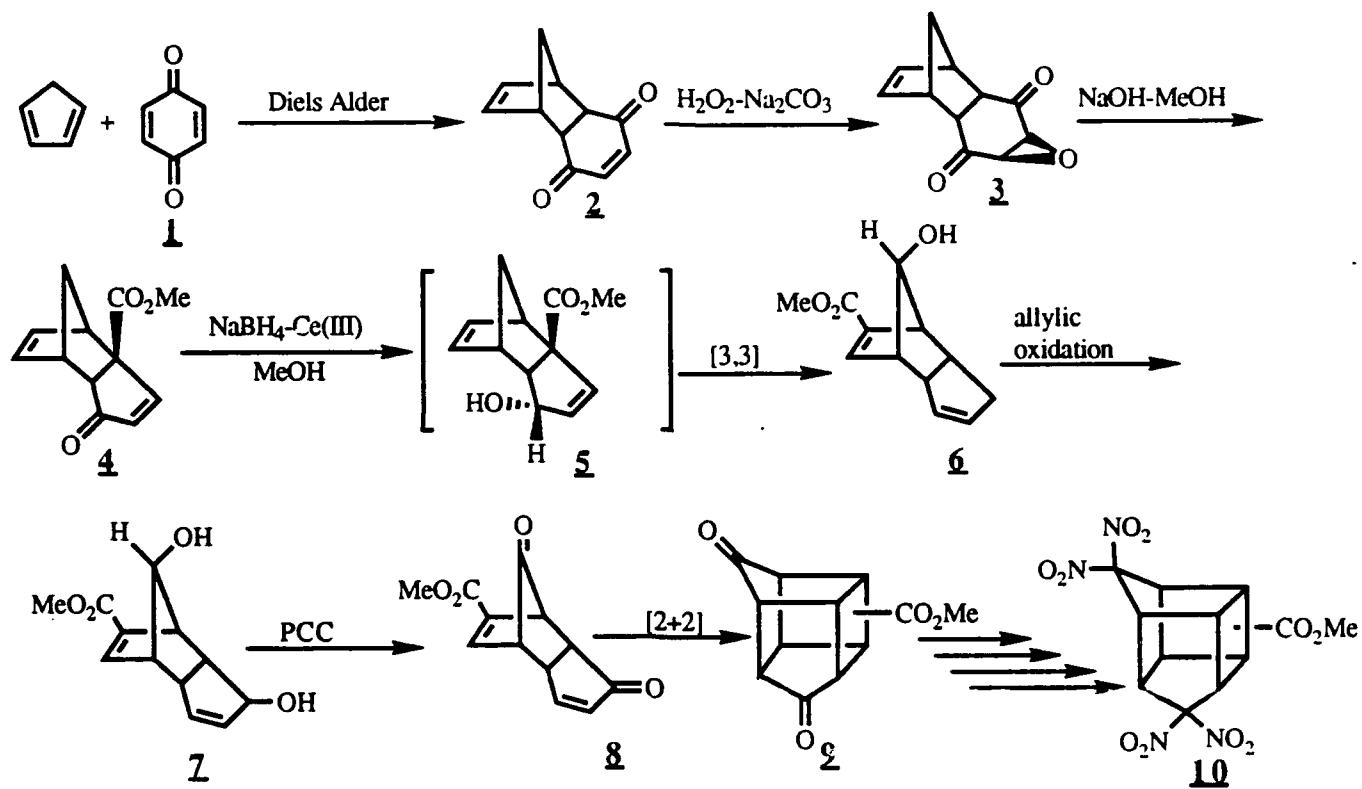
The pentanitrobishomocubane molecule 17 made by Route B is a positional isomer of caged nitro compound 10 the final product of Route A.

RESULTS AND DISCUSSIONS

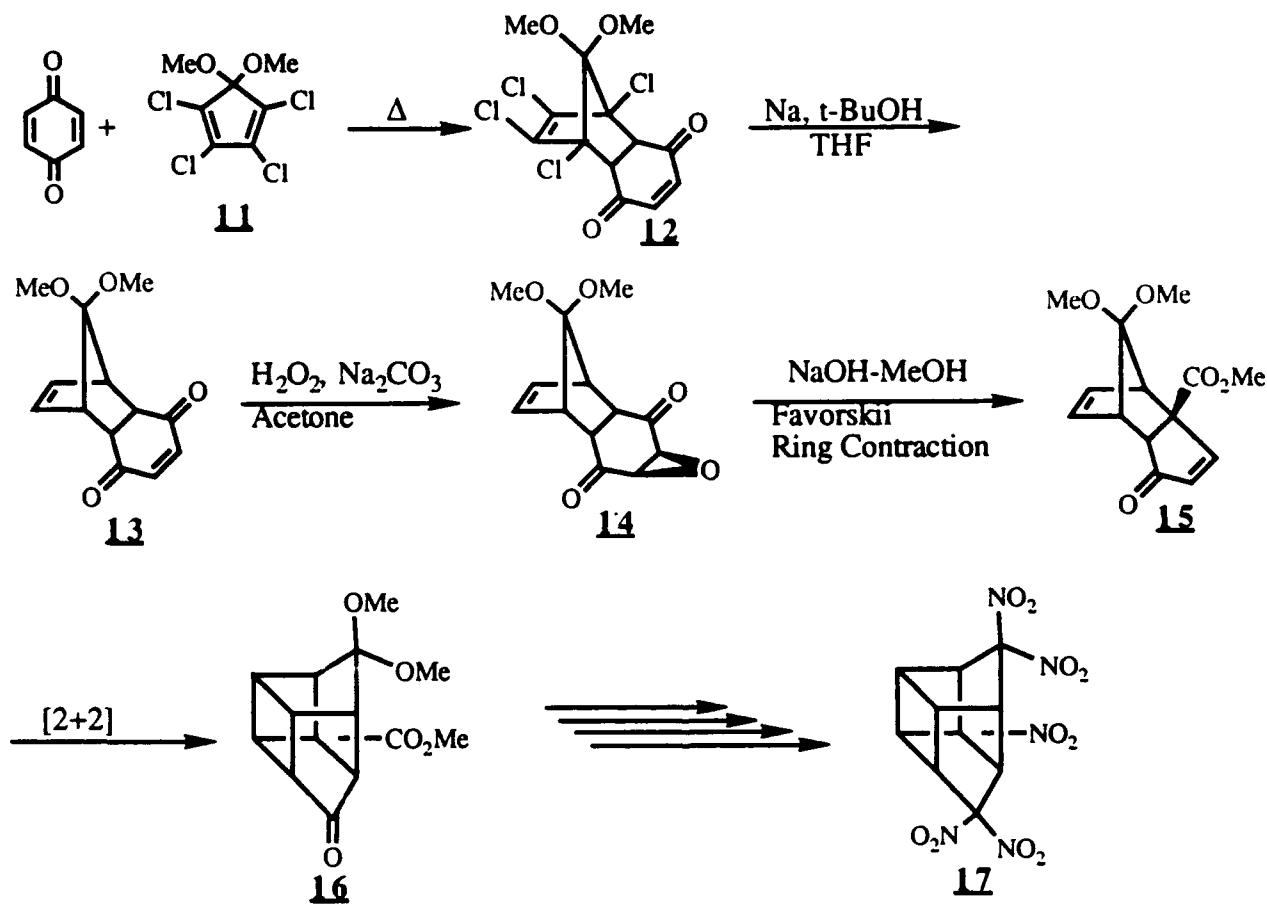
Synthetic Investigations via Route A

The Diels-Alder adduct of p-benzoquinone and cyclopentadiene afforded 2 in 90% yield. Chemoselective epoxidation of 2 with alkaline 30% hydrogen peroxide furnished 3 which on treatment with NaOH/MeOH gave exo-2-carbomethoxytricyclo [5.2.1.0^{2,6}]deca-3,8-diene-5-one 4 in 56% yield. To a solution of exo-2-carbomethoxytricyclo [5.2.1.0^{2,6}]deca-3,8-diene-5-one (4) in methanolic CeCl₃. 6H₂O (0.4M) was added sodium borohydride at 0°C. After workup and removal of solvent in vacuo, only UV active compound was isolated after silica gel chromatography using chromatotran™. The infrared absorption at 1716 cm⁻¹ reveals the presence of α,β-unsaturated ester. The olefinic region of proton resonance spectrum indicates the presence of three vinyl protons at δ 6.78(1H) and δ 5.48(2H,m). The down field vinylic proton is a part of α,β-unsaturated ester moiety and attached at β-position. The absence of bridged methylene protons further indicates the rearrangement of the original skeleton. The carbon resonance spectrum reflects the presence of four olefinic carbons, one of which (δ 135.02) is tetrasubstituted. The above key spectral features are compatible with structure 6 which is generated via [3,3] sigmatropic rearrangement of allylic alcohol 8. One step allylic oxidations that were attempted on the rearrangement product 6 are depicted in Scheme 3. Endocyclic allylic oxidations of small ring

SCHEME 1, ROUTE A

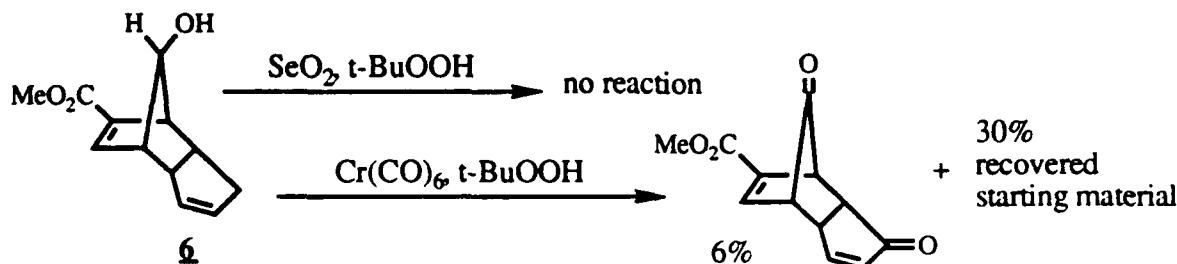


SCHEME 2, ROUTE B



systems with selenium dioxide (SeO_2) and t-butylhydroperoxide (t-BuOOH)¹³ to afford allylic alcohols are notoriously difficult¹⁴ and it was found that our system was no exception. An attempted chromium hexacarbonyl ($\text{Cr}(\text{CO})_6$)¹⁵ oxidation of 6 directly to the diketone proceeded in extremely low yield.

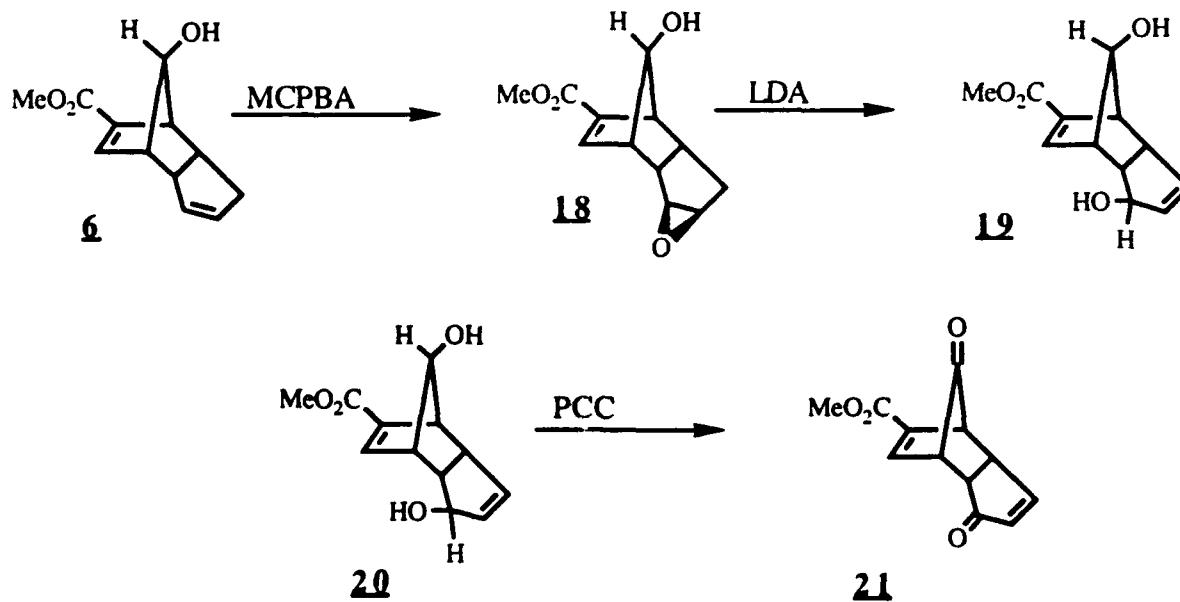
SCHEME 3



Fortunately, at this juncture, a reference noting the use of SeO_2 in refluxing dioxane/water for allylic oxidation on a system strikingly similar to the one used was discovered [11]. When compound 6 was subjected to these conditions, the coveted allylic alcohol was obtained in 48% yield! The yield can be improved with modification of the reaction conditions and method of purification. Access to the allylic alcohol 14 is crucial to the success of the synthesis of pentanitrobishomocubane shown by Route A (Scheme 1).

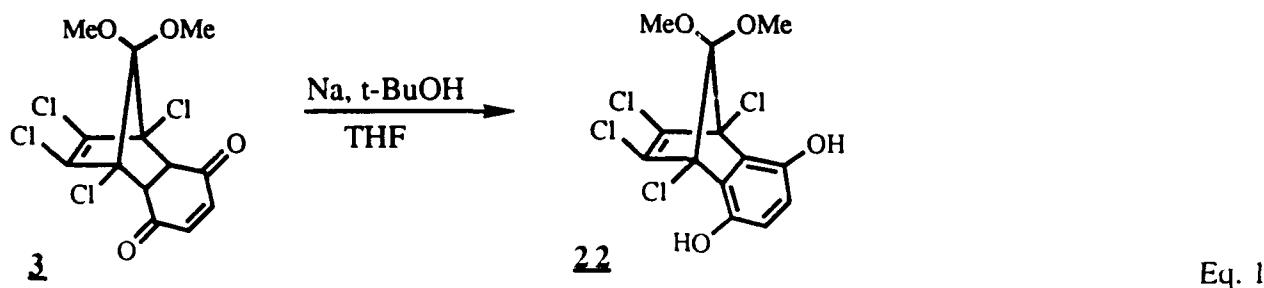
Another potential route to the isomeric diketone 21 is depicted in Scheme 4 and begins with epoxidation of 6 with m-chloroperbenzoic acid (MCPBA). Allylic alcohol 19 is expected to be the product of treatment of epoxide 18 with LDA and potassium butoxide (LIDAKOR reagent)¹⁶. Diketone 21 formed by PCC oxidation of compound 20 is an isomer of the diketone 8. The pentanitrobishomocubane ultimately formed by this route is a positional isomer.

SCHEME 4



Synthetic Investigations Via Route B

Attention was first directed toward obtaining the dechlorinated product 14. It was found that Winstein conditions afforded only the aromatized dihydroquinone 22 when 3 was refluxed with sodium, t-butanol in tetrahydrofuran (Na, t-BuOH, THF) (Eq 1). The aromatic product could be obtained in 34% yield after an hour at ambient temperature with apparently no dechlorination occurring. Formation of the dihydroquinone species could be observed by TLC at temperatures as low as -35° C. Although the dihydroquinone species could conceivably be converted back to the quinone oxidation state, this molecule would no longer be of use as it would have an additional double bond.

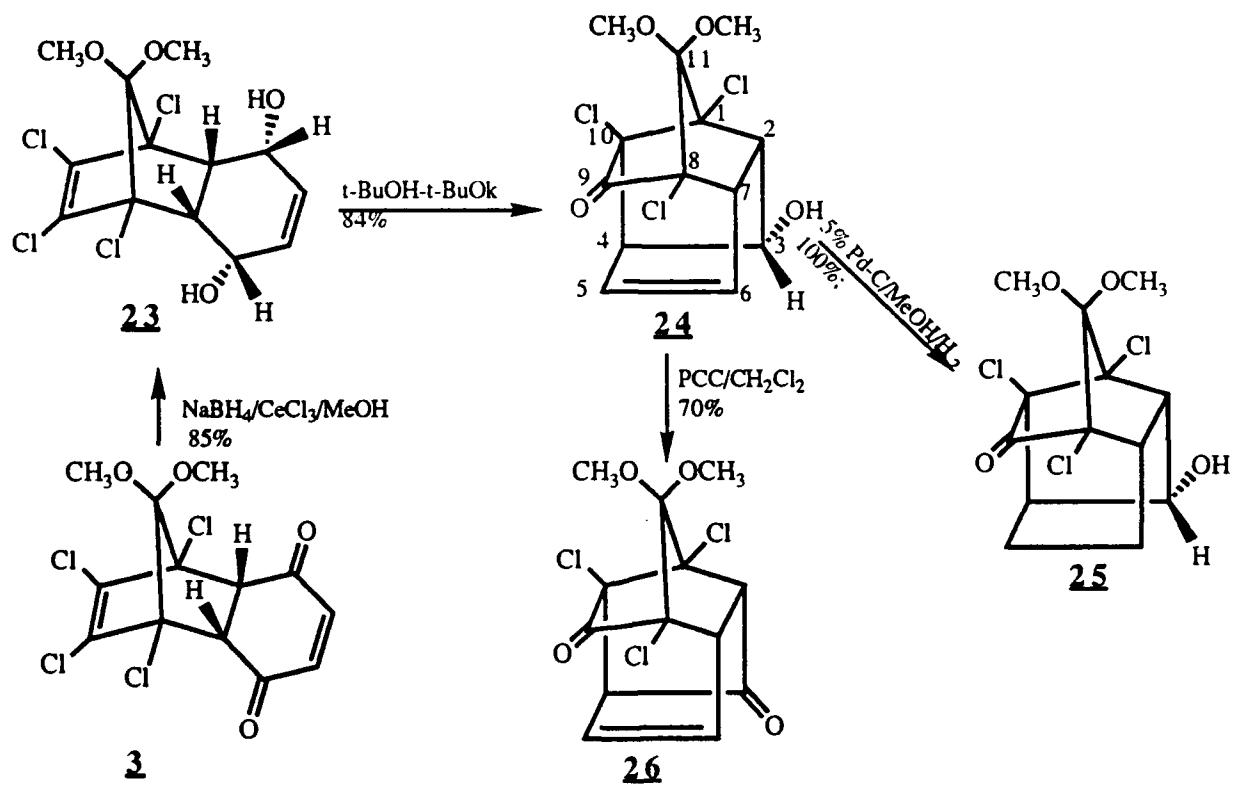


It was thought that aromatization could be prevented by attempting a dechlorination on a diol moiety, such as 23¹⁷ formed by allylic reduction of 3 with NaBH₄-Ce(III).

When a solution of 23 in butanol was treated with potassium-t-butoxide, a single product 24 was isolated in 84% yield after aqueous workup. Its infrared spectrum showed a characteristic absorption for its bridged ketone at 1791 cm⁻¹ and a broad hydroxyl absorption at 3441 cm⁻¹. The presence of the ketal group was reflected by NMR signals at δ_H 3.71(3H), 3.55(3H) and at δ_C 99.2. These observations indicated that one hydroxy group had changed to the ketone group during the course of transformation under basic conditions. The up-field signal at δ_C 193.3 of the carbonyl carbon revealed its interaction with the double bond and/or the lone pair oxygen electrons of the ketal moiety. The former possibility was eliminated because the palladium catalyzed hydrogenated product 25 still showed an up-field carbonyl signal at δ_C 195.8. It was desired to determine if the relative positions of the hydroxy group and the double bond of 23 had changed upon conversion to 24. Thus, 24 was oxidized using Swern's oxidation¹⁸ condition to form 26, which showed an olefinic resonance typical of a non-conjugated enone. The analytical and spectral data of the product 24 were consistent with the structure shown in Scheme 5.

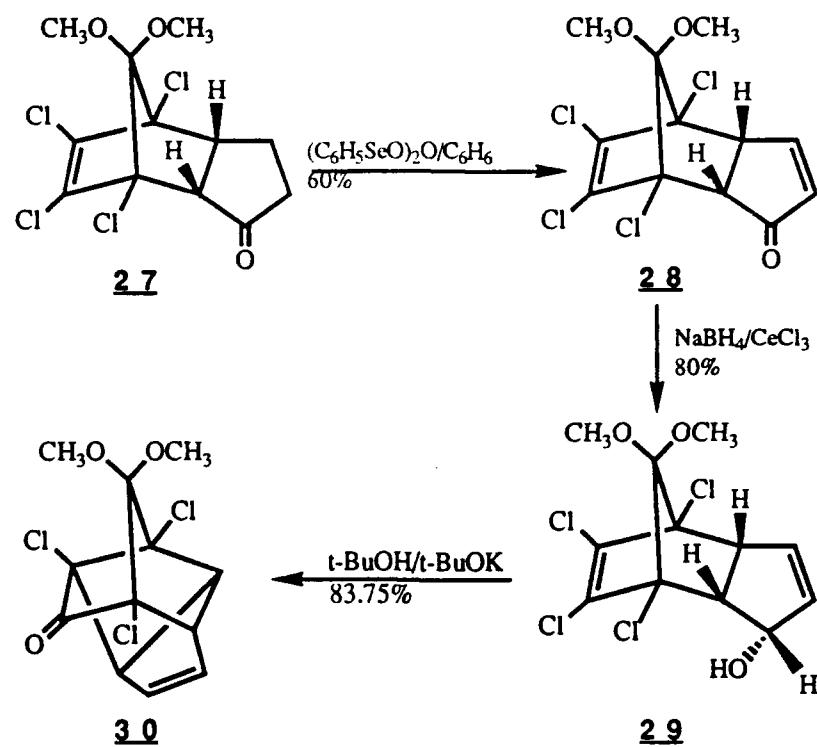
To confirm the conversion of allylic hydroxy group into a bridged ketone, 1,7,8,9-tetrachloro-3α-hydroxy-10,10-dimethoxytricyclo[5.2.1.0^{2,6}]dec-4,8-diene 29 was prepared via the illustrated reaction sequence as shown in Scheme 6. 1,7,8,9-Tetrachloro-10,10-dimethoxytricyclo[5.2.1.0^{2,6}]dec-8-en-3-one 27 was prepared according to a recently published procedure¹⁹. Treatment of a benzene solution of 27 with benzeneselenenic anhydride using Barton's procedure²⁰ furnished enone 28, b.p. 138° C./0.05 mm. Enone 28 was transformed stereoselectively to endo-allylic alcohol 29 using sodium borohydride-cerium(III) chloride heptahydrate. When 29

SCHEME 5



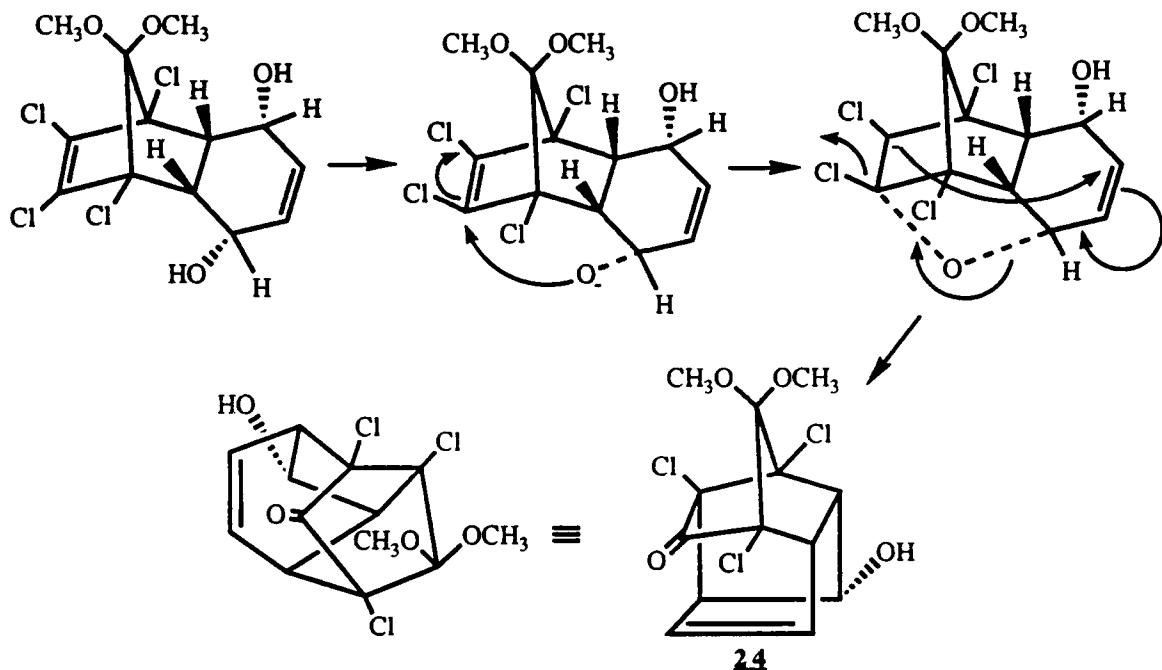
SCHEME 6

Scheme-II



SCHEME 7

Scheme-III



was treated with *t*-butanol/potassium *t*-butoxide, it was converted to a single compound 30 in 84% yield. Its infrared spectrum showed the absence of a hydroxy stretch and the presence of a strong absorption characteristic of a bridged ketone at 1785 cm^{-1} . The presence of the dimethoxyketal group was confirmed by an NMR resonance at δ_H 3.66(3H), 3.55(3H) and δ_C 106.2. One can undoubtedly infer from this experiment that the hydroxy group has been converted to a bridged ketone under basic conditions. The spectral and analytical data were compatible with structure 30.

To account for the formation of 24, a mechanism shown in Scheme 7 has been postulated. The alkoxide anion attacks the electron-deficient double bond in an intramolecular fashion, thus developing a negative charge at the vicinal carbon atom. Because of the endo-geometry of the molecule, the disubstituted double bond is attacked by the vicinal carbanion, causing a 1,2 shift of the double bond followed by cleavage of the ether linkage and elimination of chloride anion to give 24. A similar mechanism is envisioned for the formation of 30 from 29 under basic conditions.

Similar results were also obtained when 23 was subjected to Winstein's procedure of reductive dechlorination using sodium/tetrahydrofuran/*t*-butanol.

EXPERIMENTAL

1,4,4 α 8 α -Tetrahydro-endo-1,4-methanonaphthalene-5,8-di-one (2)

To a solution of p-benzoquinone (243 g, 2.25 mol) in methanol (400 ml) at -70° C was added a solution of freshly cracked cyclopentadiene (149 g, 2.27 mol) in cold methanol (100 ml). The

solution was allowed to warm to room temperature, and the product was collected by suction filtration. Yellow-brown crystals (392 g, 93%) were obtained: mp 76.0-78.5° C (lit. mp 75.8-76.2°,⁴ 77-78^o⁵); nmr (CDCl_3) δ 1.48 (m, 2H, methylene bridge), 3.28 (m, 2 H, 4a, 8a protons), 3.52 (m, 2H, bridgehead protons), 6.02 (m, 2 H, ethylene bridge protons), 6.52 (s, 2H, enone vinyl protons); ir (KBr) 3320 (w), 1660 (vs, C—O), 1601 (s, conjugated C—C), 1295 (m), 1280 (m), 1060 (m), 875, and 720 cm^{-1} (m).

exo-2-Carbomethoxytricyclo[5.2.1.0^{2,6}]deca-3,5-dien-5-one (4)

A saturated solution of sodium hydroxide in methanol was prepared by dissolving sodium hydroxide (25 g) in dry methanol (100 mL); the mixture was allowed to stand at room temperature for 2 days before use. To a warm solution of 3 (10.0 g, 52.6 mmol) in methanol (200 mL) was added to saturated methanolic sodium hydroxide solution (3.5 mL). The reaction mixture was stirred at 45° C for 1 h. The resulting highly colored solution was concentrated under reduced pressure. The viscous residue thereby obtained was diluted with water and then extracted with ether. The organic layer was washed with water until the washings became neutral. The organic layer was then dried (anhyd. Na_2SO_4) and filtered, and the filtrate was concentrated in vacuo to afford a viscous oil (ca. 7g). This material was adsorbed onto a silica gel column and eluted rapidly with 3% ethyl acetate-hexane solution. The eluate was concentrated and distilled in vacuo to afford 4 (6.0 g, 56%), bp 98° C (0.1 mm). The distillate was dissolved in hot hexane; when cooled, a colorless microcrystalline solid, mp 65° C, crystallized from solution: ^1H NMR (CDCl_3) δ 1.73 (AB, $J_{AB} = 8.9$ Hz, 1 H), 1.96 (AB, $J_{AB} = 8.9$ Hz, 1 H), 3.1–3.4 (m, 3H), 3.77 (s, 3H), 5.94 (d, $J = 5.7$ Hz, 1 H), 5.8–6.1 (m, 2H), 7.38(d, $J = 5.7$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 45.58 (d), 49.48 (d, 51.10 (t), 52.57 (q), 54.14 (d), 64.16 (s), 133.45 (d), 134.60 (d), 136.00 (d), 161.18 (d), 173.10 (s), 208.00 (s); IR (KBr) 2990 (w), 2960 (w), 1705 (vs), 1690 (vs), 1430 (m), 1220 (s), 1020 (m), 845 (m), 734 (m) cm^{-1} . Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{O}_3$: C, 70.57; H, 5.92. Found: C, 70.60; H, 6.19.

Reduction of exo-2-carbomethoxy [5.2.1.0^{2,6}]deca-3, 8-diene-5-one

Sodium borohydride (2 mmol) was added slowly to a solution of exo-2-carbomethoxy [5.2.1.0^{1,6}] deca-3,8-diene-5-one (4, 2 mmol) in methanolic $\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$ (4 ml, 0.4 M) at 0° C. The completion of the reaction was monitored by TLC. The reaction was then quenched by adding water (5 ml), and the resulting mixture was extracted with CH_2Cl_2 . The combined methylene chloride layers were washed successively with water and brine. The organic layer was then dried over anhyd. MgSO_4 . The filterate was concentrated in vacuo. The UV active compound was isolated after silica gel chromatography using chromatotranTM. The spectral and analytical characteristics are $\text{C}_{13}\text{H}_{14}\text{O}_3$, $M^+ 206$; ir(neat): 3427, 3045, 2950, 2851, 1716, 1694, 1595, 1438, 1359, 1267, 1148, 1073, 787 cm^{-1} ; ^1H NMR (CDCl_3 , 90 MHz): δ 6.77(1H, d, $J = 3.66$ Hz), 5.5(2H, m), 3.83(1H,m), 3.7(3H, s), 3.62(1H, M), 3.25–2.8(4H, m), 2.34(1H, dd, $J_1 = 10$ Hz, $J_2 = 17.5$ Hz), 1.81(1H, d with st, $J = 17.5$ Hz); ^{13}C NMR (CDCl_3 , 22.5 MHz): δ 165.12(s), 146.06(d), 135.20(s), 132.67(d), 129.67(d), 85.06(d), 51.51(q), 51.31(d), 50.86(d), 50.20(d), 37.66(d), 33.30(t).

1,2,3,4-Tetrachloro-1,4,4a,8a-tetrahydro-9,9-dimethoxy-endo-1,4-methanonaphthalene-5,8-dione (12)

A mixture of tetrachlorocyclopentadienone dimethyl acetal (52.8g,0.2 mol) and p-benzoquinone (21.6 g, 0.2 mol) was dissolved in dry toluene (100 ml) and refluxed for 24 h. The

mixture was then evaporated and the residue was recrystallized from benzene-hexane to give pale yellow crystals (1) (54 g 73%) m.p. 160.5—103° (lit 162—164°).

Reduction of 1,2,3,4-Tetrachloro-1,4,4a,8a-tetrahydro-9,9-dimethoxy-endo-1,4-methanonaphthalene-5,8-dione (12)

Enedione 11^{14,15} (3.46 g, 10 mmol) was dissolved in a solution of cerium chloride heptahydrate (7.5 g, 20 mmol) in methanol (35 mL), and its reduction with sodium borohydride (750 mg, 20 mmol) was allowed to proceed in the manner described above for the corresponding reduction of 1. The product, 23 (2.1 g, 60% g), was recrystallized from ethyl acetate–hexane mixed solvent to afford a colorless microcrystalline solid: mp 167–168° C; IR (KBr) 3400 (s), 740 cm⁻¹ (s); ¹H NMR (Me₂SO-d₆) δ 2.47 (m, 4H), 2.98 (s, 3H), 3.07 (s, 3H), 3.87 (s, 2H), 5.53 (s, 2H); ¹³C NMR (Me₂SO-d₆) δ 50.1 (q), 51.4 (q), 52.1 (d), 61.9 (d), 76.6 (s), 113.8 (s), 128.5 (s), 132.8 (d); MS (70 eV), m/e (relative intensity) (no molecular ion), 345.0 ([M – Cl]⁺, 0.4), 57.0 (100.0). Anal. Calcd for C₁₃H₁₄Cl₄O₄: C, 41.52; H, 3.75. Found: C, 41.76; H, 3.79.

Rearrangement of Diol (23)

To a mixture of t-BuOH (10 ml) and t-BuOK (500 mg) was added diol 23 (0.75 g, 2 mmol) at room temperature. The reaction mixture was stirred at room temperature for 18 hrs. when TLC showed absence of starting material. The reaction mixture was poured on crushed ice and extracted with methylene chloride (100 mL). The organic layer was washed with water, brine, and dried over anhyd. Na₂SO₄. Removal of solvent furnished solid which was crystallized from CH₂Cl₂-hexane mixture to furnish pure 24 (0.57 g), m.p. 118° C, IR(KBr): 3441, 2991, 2952, 1791, 1217, 1097, 890, 765, 733, 720, 698 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 6.43 (1H, dt, J₁ = 7.8 Hz, J₂ = 1.5 Hz), 5.99 (1H, m), 3.94 (1H, dd, J₁ = 8.3 Hz, J₂ = 2 Hz), 3.71 (3H, s), 3.55 (3H, s), 3.38 (1H, ddd, J₁ = 9.3 Hz, J₂ = 5.6 Hz, J₃ = 1.5 Hz), 3.18 (1H, m), 3.09 (1H, ddd, J₁ = 9.3 Hz, J₂ = 3.6 Hz, J₃ = 2.2 Hz), 2.94 (1H, d, J = 8.3 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 193.3, 137.4, 128.4, 99.2, 83.5, 83.4, 82.7, 80.1, 61.7, 54.2, 52.0, 47.8, 47.1. Anal. Calcd. for C₁₃H₁₃Cl₃O₄: C = 45.98, H = 3.86, Cl = 31.32; Found C = 45.76, H = 3.88, Cl = 31.67.

Hydrogenation of rearranged product 24

A heterogeneous mixture of methanolic solution of 23 (0.34, 1mmol) and 5% Pd-C (20 mg) was taken in a flask. The reaction flask was evacuated and filled with hydrogen using hydrogen hallow. The mixture was stirred under hydrogen overnight and filtered through a pad of celite. The filterate was concentrated to furnish quantitative yield of hydrogenated 25, m.p. 149–50° C. The spectral characteristics of 25 are IR(KBr): 3433, 2953, 2893, 2842, 1788, 1458, 1215, 1101, 1078, 1045, 1030, 970, 889, 655 cm⁻¹; ¹H NMR (90 MHz, CDCl₃): δ 4.33(1H, bd, J = 5.7 Hz), 3.67(3H, s), 3.56(3H, s), 3.29(1H, ddd, J₁ = 10.6 Hz, J₂ = 3.52 Hz, J₃ = 1.76 Hz), 2.61–2.96(3H, m), 1.48–2.01(4H, m); ¹³C NMR(22.6 MHz, CDCl₃): δ 195.8, 102.4, 82.9, 79.3, 78.1, 77.7, 57.7, 52.3, 52.2, 51.9, 46.2, 26.2, 15.7; GC-MS (70 ev): m/z 305(M⁺-HCl).

Swern's oxidation of rearranged product 24

Oxalylchloride (0.45 mL, 5.1 mmol) dissolved in dry methylene chloride (10 mL) was placed in a three neck flask equipped with thermometer and pressure-equalizing addition funnel. A mixture of DMSO (0.8 mL, 11.1 mmol) in CH₂Cl₂ (3 mL) was added into the flask dropwise at -

70° C. Stirring was continued for 10 min. followed by the addition of 24 (1.7 g, 5 mmol) in CH₂Cl₂ (5 mL). The reaction mixture was stirred for 15 min and triethylamine (2.5 g, 25 mmol) was added at 70° C. The cooling bath was removed and the reaction mixture was brought to room temperature when water (10 mL) was added. The organic layer was removed and the aqueous layer was re-extracted with CH₂Cl₂. The organic layer was continued, washed with dil HCl, followed by aq. NaHCO₃, water and brine. The organic layer was dried over anhyd. Na₂SO₄. Removal of solvent furnished solid which was crystallized from CH₂Cl₂-hexane mixture to furnish 87% of 26, m.p. 151-52° C. The spectral characteristics are IR(KBr): 2953, 1798, 1770, 1206, 1145, 1110, 1090, 972, 711 cm⁻¹; ¹H NMR(300 MHz, CDCl₃): δ 6.42(1H, dt, J₁ = 8 Hz, J₂ = 1.65 Hz), 6.27(1H, dd, J₁ = 8 Hz, J₂ = 5.8 Hz), 3.71(3H, s), 3.6(3H, s), 3.3(1H, dd, J₁ = 8 Hz, J₂ = 5.8 Hz), 3.22(1H, dd, J₁ = 9.2 Hz, J₂ = 2.9 Hz); ¹³C NMR(75 MHz, CDCl₃): δ 200.7, 191.6, 135.5, 132.8, 102.5, 83.4, 76.5, 73.5, 58.5, 53.1, 52.3, 52.1, 49.8. Anal. Calcd. for C₁₃H₁₁Cl₃O₄: C = 46.25, H = 3.28, Cl = 31.5; Found C = 46.28, H = 3.42, Cl = 31.52.

1,7,8,9-Tetrachloro-10,10-dimethoxytricyclo[5.2.1.0^{2,6}]dec-8-ene-3-one 27

Tetrachlorocyclopentadienone dimethyl acetal (13.5 g), 2-cyclopentenone (4.2 g), and a trace of hydroquinone were heated under an atmosphere of argon in a sealed tube at 115° C for 75 h. The reaction mixture was purified by flash chromatography with petroleum ether: diethylether yielding 27 (13.6 g; 79%; white crystals, m.p. 68-74° C). IR(CCl₄) (cm⁻¹): 1750, 1602. ¹H NMR (CDCl₃δ): 1.95-2.32(br.m)(4H) C-H(4.5); 3.14(d)(1H) J_{2,6} = 9 Hz C-H(2); 3.42(m)(1H) J_{6,2} = J_{6,5_{exo}} = 9 Hz, J_{6,5_{endo}} = 4 Hz C-H(6); 3.56(s)(3H) OC-H₃; 3.62(s)(3H) OC-H₃. ¹³C NMR (CDCl₃) δ: 19.0 C-5; 38.4 C-4; 48.9 C-6; 51.8 OCH₃; 52.7 OCH₃; 57.4 C-2; 76.0 C-7; 77.9 C-1; 114.5 C-10; 129.0 and 129.2 C-8 and C-9; 213.3 C-3. MS: 346 (M⁺)(0.6%), 344(M⁺)(0.3%); 311(100%), 309(M⁺-Cl)(100%); 273(M⁺-Cl-HCl)(22%).

Oxidation of 1,7,8,9-Tetrachloro-10,10-dimethoxytricyclo [5.2.1.0^{2,6}]dec-8-ene-3-one

A mixture of 27 (1 g, 2.89 mmol), benzene selenic anhydride (1.15 g, 1.1 Eq) was taken in dry benzene (10 ml) and refluxed for 2 hrs when TLC showed an absence of starting material. The mixture was charged on silica gel columns and elution with 15% hexane furnished enone 28, (0.6 g) in 60% yield. The spectral characteristics are IR (KBr) 2985, 2951, 1718, 1583 cm⁻¹ ¹H NMR (CDCl₃): δ 7.5(1H), 6.25(rH), 3.85(1H), 3.65(3H), 3.55(3H), 3.16(1H) ¹³CNMR (CDCl₃): δ 202, 158, 139, 130, 127.7, 115, 76.8, 75, 55, 53, 5, 52.7, 51.8.

Reduction of 28

Enone (0.495, 1.44 mmol) was dissolved in a methanolic solution of 0.4M. Cerium chloride heptahydrate (3.5 mL). The reaction mixture cooled to 0° C when sodium borohydride (55 mg) was added. The reaction mixture was allowed to stir until TLC showed an absence of starting material. The reaction was quenched via addition of water (5mL), and the resulting mixture was extracted with ether. The combined organic layer was washed with water, brine, and dried over anhyd. Na₂SO₄. Removal of solvent furnished allylic alcohol 29 in 80% yield. The spectral characteristics are ¹H NMR (CDCl₃): δ ¹³(NMR(CDCl₃):δ 137.9, 129, 128.3, 128.2, 115.1, 77.3, 76.5, 75.7, 61.1, 52.4, 51.6, 51.5.

Rearrangement of 29

Allylic alcohol 29 (0.307 g, 0.88 mmol) was added to a mixture of t-BuOH (10 mL) and t-BuOK (0.11 g, 1 mmol). The reaction mixture was stirred at room temperature overnight. The reaction mixture was poured on crushed ice and extracted with CH₂Cl₂ (25 mL). The organic layer was washed with 1% dil HCl followed by aqueous NaHCO₃, water, brine, and dried over anhyd. Na₂SO₄. Removal of solvent furnished solid 30 (84%) which was crystallized from CH₂Cl₂-hexane, m.p. 125-26° C. The spectral characteristics are IR(KBr) 2949, 1785, 1218, 1207, 1122, 1093, 769, 754 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ 6.35(1H, dd, J₁ = 5.7 Hz, J₂ = 2.6 Hz), 6.14 (1H, dd, J₁ = 5.7 Hz, J₂ = 2.8 Hz), 3.66(3H, s), 3.55(3H, s), 3.39-3.71(2H, m); ¹³C NMR(50 MHz, CDCl₃): 191.9, 138.9, 135, 106.2, 83.9, 74.4, u70.3, 55.7, 55.5, 53.0, 52.0, 52.1; GC-MS (70 ev): m/z = 309 (M⁺).

CONCLUSIONS

Treatment of 1, 8, 9, 10-tetrachloro-3α, 6α-dihydroxy-11,11-dimethoxytricyclo [6.2.1.0^{2,7}]undec-4,9-diene and 1, 7, 8, 9-tetrachloro-3α-hydroxy-10,10-dimethoxy[5.2.1.0^{2,6}]dec-4,8-diene with potassium-t-butoxide/t-butanol furnished two new tetracyclic compounds 1,8,10-trichloro-11,11-dimethoxy-3α-hydroxytetracyclo[6.2.1.0^{2,7.0^{4,10}] undec-5-ene-9-one and 1,7,9-trichloro-8,8-dimethoxytetracyclo[5.3.0.0^{2,6.0^{5,9}]dec-3-en-10-one respectively via base eliminative cyclization.}}

It is also envisaged that substituted tetracycloundecanes are viable precursors to pentacyclo-undecane and pentaprismane.

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